

REFLECTANCE SPECTRA OF MAFIC SILICATES AND PHYLLOSILICATES FROM .6 TO 4.6 μ m;

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INTRODUCTION Spectral reflectance, obtained by spacecraft and earth-based telescopic observations, is the dominant method of collecting mineralogical information concerning the surface properties of solar system objects. Our ability to interpret this data, in terms of the identity and abundance of minerals present on a surface, is important for addressing more general questions concerning the origin and evolution of that body as well as the solar system as a whole. The reflectance of geologically important materials in the 0.3 to 2.5 μ m wavelength region has been the subject of intense laboratory research for many years(1,2,3,4,5). However, there has been a paucity of research concerning the reflectance behavior of geologic materials in the 2.5 to 4.6 μ m wavelength region.

The mapping spectrometers on future spacecraft missions, such as Galileo and the Mars Orbiter, are designed to return spectral reflectance data from 0.7 to 5.2 μ m. Thus, it is important for interpretation of such data to expand laboratory reflectance measurements to include the longer wavelength region. The study presented here provides empirical laboratory data concerning the reflectance behavior of geologically important materials in the 2.5 to 4.6 μ m wavelength region.

EXPERIMENTAL METHOD For this study two infrared, cooled, circular variable filter (CVF) spectrometers with InSb detectors were used and the combined wavelength coverage spanned the .65 to 4.5 μ m wavelength region. In both instruments the detector, filter, and other internal components are operated at liquid nitrogen temperature (77 K). The spectral resolution ($\Delta\lambda/\lambda$) of both CVF's is about 1.5%.

The mafic samples were chosen to represent minerals which result in mafic to ultramafic assemblages. All the mafic samples were dry sieved to the <38 μ m grain size. The phyllosilicates were chosen to represent a variety of structural types and amounts of natural hydration states. All phyllosilicate samples were dry sieved to the 38-45 μ m grain size. Additionally, a palagonite was included in the sample suite since this material has been suggested as a Mars soil analog material(6,7). The 2-3 μ m grain size of the palagonite was separated by liquid suspension in methanol.

All samples were placed in a furnace prior to being situated in an environment chamber. The environment chamber was flushed with inert nitrogen gas during the entire data collection and heating sequence. The samples were allowed to equilibrate in the nitrogen environment for thirty minutes before room temperature spectral data were collected. The samples were then heated at 200°C for thirty minutes and subsequently allowed to cool to room temperature before additional data were collected.

BACKGROUND Electronic transitions of the first transition element series, especially the petrologically significant cations Fe^{2+} and Ti^{3+} , result in absorptions in the visible and near-infrared (0.3 to 2.5 μ m) region of the electromagnetic spectrum(8), and are due to ions located within specific crystallographic sites. Hence, from the spectra direct information is obtained concerning the chemistry and crystal structure of the material.

For the silicates and of this study, the most important species which have vibrationally induced absorptions are the H_2O molecule and the OH^- ion. The H_2O molecule has strong absorption features located near 2.9 μ m (O-H asymmetric stretch), 3.0 μ m (H-O-H bend overtone), and 3.1 μ m (O-H symmetric stretch)(9). Overtones and/or combinations of these bands can occur near 0.94, 1.135, 1.38, 1.45, and 1.88 μ m(9). There is a fundamental of the OH^- group located near 2.75 μ m and the first overtone is located near 1.4 μ m(9). Additionally, bands in the 2.2 to 2.4 μ m region involve a combination of the OH^- fundamental with a X-OH bending mode (where X is usually Al or Mg)(9).

DISCUSSION The results of the spectral measurements for the mafic silicates are presented in Figures 1 to 3. All spectra, except the plagioclase, exhibit electronic absorptions located near 1 and/or 2 μ m which are due to Fe^{2+} located in octahedral crystallographic sites. These absorptions remain unchanged after heating. Additionally, all spectra have an absorption centered near 3 μ m which is due to H_2O . This absorption changes in intensity, and in some cases shape, after heating. We believe these changes represent the removal of physically adsorbed H_2O from the sample. The continued presence of the 3 μ m band in the spectra of all samples after heating implies that H_2O bearing contaminants are present, or alternatively, the samples

contain fluid inclusions.

The results of the spectral measurements for the phyllosilicates are presented in Figures 4 and 5. Kaolinite and pyrophyllite have types of structures which typically accommodate little cationic substitution and hence do not incorporate interlayer $H_2O(10)$. Before and after heating, the spectra of both samples exhibit strong absorption bands located near $2.75\mu m$, due to OH^- , and the spectra after heating show minor changes due to the removal of physically adsorbed H_2O . This spectral behavior is illustrated in Figure 4 for kaolinite.

The Na-Montmorillonite (Fig. 5) has a structure which has abundant cationic substitution and its open nature results in the presence of interlayer $H_2O(10)$. The spectrum of the sample before heating exhibits a broad $3\mu m$ band and narrower but pronounced $1.9\mu m$ band both due to H_2O and bands located near 1.4 and $2.8\mu m$ both due to OH^- . After heating, the spectrum exhibits the effects of removing the physically adsorbed, and possibly some of the interlayer, H_2O . The 1.9 and $3.0\mu m$ bands have decreased in intensity, while the band near $2.8\mu m$ has become more pronounced.

The palagonite spectrum (Fig. 6) before heating shows a strong, broad $3\mu m$ absorption and a weak absorption near $1.9\mu m$, both indicate the presence of H_2O . After heating, the spectrum shows virtually no $1.9\mu m$ band and the $3\mu m$ band although slightly reduced in intensity still remains very prominent. We believe the physically adsorbed H_2O has been removed, so the continued presence of the $3\mu m$ band indicates abundant H_2O . The spectral behavior of the $3\mu m$ band is reminiscent of the plagioclase.

CONCLUSIONS This study has provided valuable spectral reflectance information about mafic silicates and phyllosilicates in the 2.5 to $4.6\mu m$ wavelength region. In this wavelength region we have shown that the reflectance of these materials is strongly affected by the presence of H_2O and OH^- . Therefore, the identification of these absorbing species is greatly enhanced.

The reflectance behavior of mafic silicates beyond $2.5\mu m$ can provide additional information about the chemical composition of the pyroxenes by revealing the long wavelength edge of the clinopyroxene absorption band located near $2\mu m$. For Mercury, the Moon, Earth, Mars, and the asteroids this provides additional information which enhances our ability to map changes in the mineral composition and abundance across the surface of a planetary body.

The reflectance of phyllosilicates beyond $2.5\mu m$ provides additional information concerning the potential for identifying compositional and water content variations of these minerals. Since OH^- is structurally bound to octahedrally coordinated cations in phyllosilicates, the substitution of various cations should result in the shifting of absorptions due to the OH^- -metal vibrations. Additionally, absorptions due to interlayer H_2O can be expected to vary as a function of amount of water available on the surface. In the case of Mars, a map of water content variation could identify possible sources and/or sinks of weathering products on a global scale and allow the study of water transport on the surface.

The spectral reflectance behavior of the palagonite beyond $2.5\mu m$ implies that the water contained within the sample is not composed solely of physically adsorbed water. Thus, the palagonite, if located in the desiccated Martian environment, could provide an exchange mechanism for atmospheric water vapor by trapping and releasing physically adsorbed water. The palagonite, during its initial formation, also provides a more permanent mechanism for removal of atmospheric water from the Martian environment.

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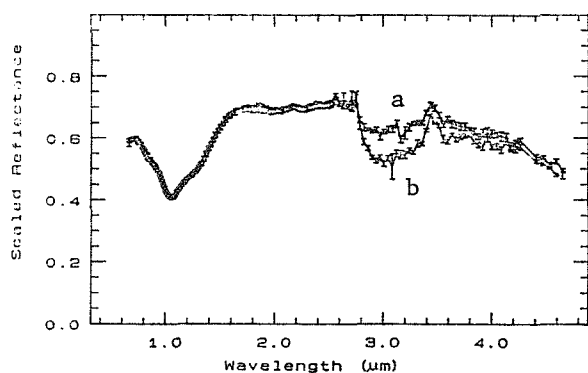


Figure 1. Reflectance spectra of olivine (Fo_{89}) before (b) and after (a) heating. The absorption centered near of $1\mu\text{m}$ is due to the presence of Fe^{2+} and is unaffected by heating. The decrease of the absorption located near $3\mu\text{m}$ upon heating is due to the loss of physically adsorbed H_2O .

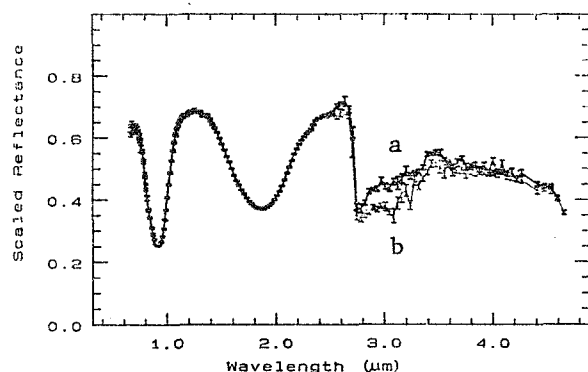


Figure 2. Reflectance spectra of orthopyroxene (En_{86}) before (b) and after (a) heating. The absorptions located near 1 and $2\mu\text{m}$ are due to the presence of Fe^{2+} and are not affected by heating. Because this sample contains tremolite as a contaminant, after heating the $3\mu\text{m}$ band depth decreases, due to the loss of physically adsorbed H_2O , and the relatively narrow absorption located near $2.75\mu\text{m}$, due to OH^- , is more pronounced.

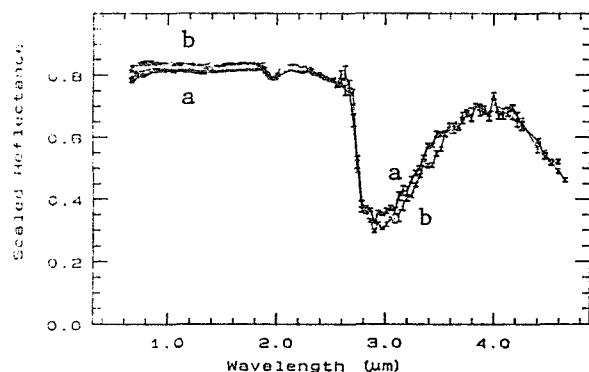


Figure 3. Reflectance spectra of plagioclase (An_{55}) before (b) and after (a) heating. The spectra of this mineral exhibit the strongest $3\mu\text{m}$ of all the mafic silicates due to the presence of fluid inclusions in the sample. Since the H_2O in the fluid inclusions is not easily lost upon heating, the minor spectral changes indicate solely the loss of physically adsorbed H_2O .

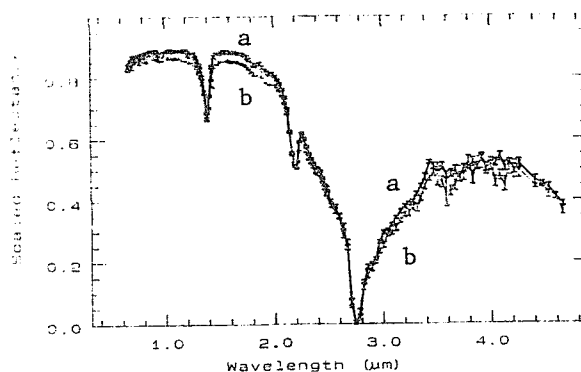


Figure 4. Reflectance spectra of kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) before (b) and after (a) heating. The spectra exhibit OH^- vibrational absorptions near 1.4 , 2.2 , and $2.75\mu\text{m}$. The spectral changes due to heating indicate the loss of physically adsorbed H_2O .

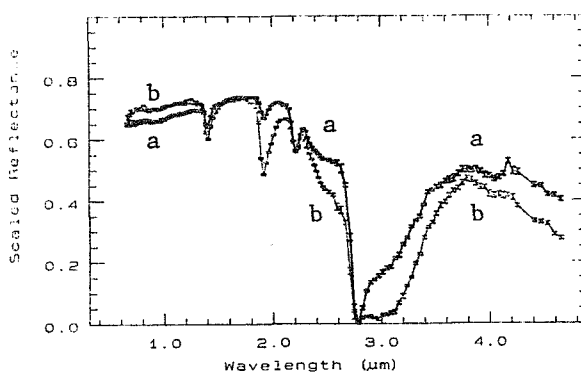


Figure 5. Reflectance spectrum of Na-Montmorillonite (nominally, $(\frac{1}{2}\text{Ca,Na})_{0.7}(\text{Al,Mg,Fe})_4[(\text{Si,Al})_8\text{O}_{20}](\text{OH})_4 n\text{H}_2\text{O}$) before (b) and after (a) heating. Before heating the spectrum of this sample exhibits absorptions due to H_2O near 1.9 and $3.0\mu\text{m}$ and OH^- near 1.4 and $2.2\mu\text{m}$. After heating the spectrum exhibits the effects of removing physically adsorbed, and potentially inter-layer H_2O , by the reduced intensity of the 1.9 and $3.0\mu\text{m}$ bands and the OH^- band near $2.8\mu\text{m}$ is more pronounced.

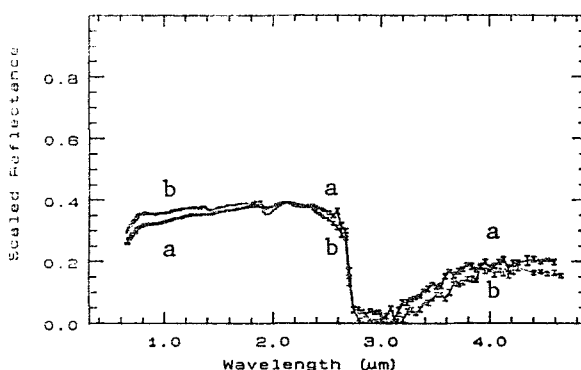


Figure 6. Reflectance spectrum of palagonite before (b) and after (a) heating. Before heating the spectrum of this sample exhibits a weak $1.9\mu\text{m}$ band and a strong $3\mu\text{m}$ band both indicative of H_2O . After heating the spectrum exhibits a very weak $1.9\mu\text{m}$ band implying removal of H_2O , yet the $3\mu\text{m}$ band remains prominent. This spectral behavior is very reminiscent of the plagioclase.